Our study includes a novel process for the synthesis of conductive polyaniline; named self-oxidation polymerization. Spinel LiNi$_{0.45}$Th$_{0.05}$Mn$_{1.5}$O$_4$ (LNMO) and LiNi$_{0.45}$Th$_{0.05}$Mn$_{1.5}$O$_4$ (LNMO-Th) have been prepared by a sol-gel auto-combustion process. The well crystalline spinel Fd-3 m structures with a high degree of disordering with Th- substituted samples were obtained. The LNMO sample's particle morphology demonstrated a consistent octahedron-like form with a wide range of size distributions. The Th- doped LNMO samples, on the other hand, consisted of bigger, flattened particles with fewer facets and a smaller distribution of particle sizes. LiNi$_{0.45}$Th$_{0.05}$Mn$_{1.5}$O$_4$/Polyaniline composite (LNMO-Th-PA) was prepared for the first time by self-oxidation polymerization through the composite material itself without using any external oxidant. FT-IR, XRD and HR-TEM were utilized to assess the structural characteristics. The element valence variations were done using XPS spectroscopy. The chemical compositions were consistently distributed throughout the samples, according to EDX spectroscopy. The optical properties show that all samples have low band gap values. Thus, the synthesized materials are semiconductor materials and they can be used in photoelectric devices.

**Keywords**: Disordered spinel, Auto-combustion synthesis, Cationic substitution, Cathode materials.

1. **INTRODUCTION**

Lithium-ion batteries (LIBs) that use a conductive polymer as the positive electrode have drawn a significant amount of interest ever since MacDiarmid and Heeger's [1] presentation of the electrochemical doping of polyacetylene. The main performance index of these energy devices is thought to be primarily determined by the characteristics of the electrode materials used in LIBs [2]. Doped polymers can be used widely in a variety of fields, such as LIBs, supercapacitors, lithium-sulfur
batteries, and other devices because they possess the electrical conduction properties of metals, the flexibility and processability of organic polymers, as well as the ability to switch back and forth between conductive and insulating states [3]. Due to its high thermal and environmental durability, straightforward manufacturing, deviating redox chemistry, and distinctive doping/de-doping mechanism, polyaniline (PANI) offers more benefits over other conducting polymers. Conducting polyaniline can overcome the drawbacks of electrode materials such as weak electron conductivity, and a slow lithium ion transfer rate thanks to their unusual electrical properties and distinctive physicochemical traits. The quick attenuation of capacity may be brought on by the substantial volume change reducing electrical contact between the active materials and the current collector. The specific capacity of electrode materials is decreased, especially at high rates, by poor electron conductivity and sluggish Li\(^+\) diffusion rate [4]. The spinel (LNMO) material exhibits significant potential in the specimens for applications as cathodes for rechargeable LIBs in plug-in hybrid electric vehicles (PHEV) [5, 6]. Finally, structural disturbance at large potential sites (> 4.5 V vs. Li) during charge/discharging operations has been discovered to be resistant to the LNMO [7, 8]. The disordered Fd-3m spinel phase demonstrates improved electrochemical activity and cycling stability than the ordered P4332 phase due to topotactic phase transitions for the couples Mn\(^{2+/3+}\), Ni\(^{2+/3+}\), and Ni\(^{3+/4+}\) that occur at 4, 4.7, and 4.8 V, respectively [9–11]. Several surveys have been conducted to investigate the impact of the substitution of Nickel ions with Zinc, Cobalt, Iron, Chromium, Copper, and Titanium on the electrochemical and structural characteristics to regulate the 16d sites' cation ordering, and prevent the Li\(_x\)Ni\(_{1-x}\)O defective phase from forming [12–18]. In this regard, LiNi\(_{0.45}\)Co\(_{0.1}\)Mn\(_{1.45}\)O\(_4\) was shown to have the greater specific capacity and capacity retention than LNMO at the C/5 rate by Jing Mao et al. [19]. In addition, a different team of researchers has created the spinel formula LiNi\(_{0.4}\)Fe\(_{0.2}\)Mn\(_{1.4}\)O\(_4\), which has an initial specific capacity (134mAh/g) better than LNMO materials [20]. In fact, altering the synthesis procedures and their additions, such as the molten salt approach [21, 22], solid-state method [23], sol-gel method [24, 25], microwave-assisted method [10, 26], and co-precipitation [7] have had a significant impact on the electrochemical and physicochemical characteristics of pure and doped spinel LNMO. However, sol-gel combustion formulation was found to be more favorable due to the excellent end-product homogeneity and the effective control it provides on the stoichiometric [27].

2. EXPERIMENTAL

2.1. Materials

In this work, analytical-grade chemicals including lithium carbonate, manganese acetate tetrahydrate, nickel acetate tetrahydrate (Sigma-Aldrich), and thorium nitrate hydrate (Hayashi). Additionally, the entire investigation was conducted with deionized water.
2.2. Procedure

2.2.1. Preparation of LNMO and LNMO–Th.

Utilizing glycine as a chelating agent, the precursor for the as-prepared nanostructured LNMO was made using the sol-gel auto-combustion process. Lithium carbonate, manganese acetate tetrahydrate, nickel acetate tetrahydrate, and glycine were dissolved in water (deionized) in stoichiometric proportions to create the precursor. The molar ratios of Li: Ni: Mn were 2:1:3. To make up for the lithium evaporating during calcination, 5% more lithium was added. Also, Glycine was mixed in a 1:1 molar ratio with Li⁺. The aqueous solution was heated to 90 °C for 90 minutes after stirring magnetically for 10 minutes at room temperature. To evaporate the extra water, the solution's temperature was raised to 140 °C, progressively increasing the viscosity of the mixture. When the solution temperature reached 180 °C, a substantial frothy mass developed. Further raising the temperature caused the viscous gel to self-combust, resulting in a black, spongy precursor that was left to dry overnight at 100 °C in an oven. The ground precursor was subjected to two phases of calcination at 400 °C for three hours and 750 °C for three hours, respectively, to produce the finished LNMO nanopowders. A sample of LiNi₀.₄₅Th₀.₀₅Mn₁.₅O₄ (LNMO-Th) was made in the same manner.

2.2.2. Preparation of LNMO–Th-PANI Composite.

In situ chemical polymerization was used to create the LNMO-Th-PA composite [28]. 160 ml of aniline solution received 10 mmoles of HCl while being stirred in an ice bath for one hour at 0 °C. An aniline-HCl solution was constantly poured into the suspension while being swirled with a magnetic stirrer to achieve homogenous dispersion. 1% of LNMO-Th powder was added to distilled water and mixed for one hour. PPS was utilized as an oxidant to start the polymerization process in the referenced article. In contrast, no external oxidant was used to perform polymerization in our investigation, which was a first. Aniline-HCl solution's color changed to green after LNMO-Th was added, indicating that the polymerization process was initiated by self-oxidation and that LNMO-Th serves as an oxidant. By keeping the samples agitated at 0 to 5 °C for 24 hours, the polymerization process was completed. Following the earlier section, the produced yield was cleaned. The coated nanoparticles were repeatedly washed in huge quantities of ethanol and distilled water until the filtrate, as measured by the suction filter, was colorless. The wet LNMO-Th-PA composites were then dried for 12 hours at 60 °C in a vacuum oven.

2.3. Physical measurements

X-ray diffraction (XRD) was used to evaluate the final products using a Bruker AXS diffractometer model with a Cu-K radiation source (=1.54056 A) at 10-80° (2θ range), 40 mA and 40 kV (D8-ADVANCE, Germany). On a Vector-22 (Bruker, Germany) instrument, Fourier transform infrared spectroscopy (FT-IR) was utilized to detect the structural characteristics of various items. High Resolution Transmission Electron Microscopy (HR-TEM), a TECNAI G2 microscope (at 200
kV), was used to analyze the microstructure features. By the integrated Energy Dispersive X-ray Spectroscopy (EDX) tool, the elemental makeup of each sample was identified.

2.4. Electrical and electrochemical characterization

Each powder sample was ground for two hours at 500 rpm in a planetary micro mill (FRITSCH, Pulverisette 7). Uniaxial dry pressing of powders without the use of a binder in a steel die with a 12.5 mm diameter produced the compressed pellets. As electrodes for electric and dielectric tests using the SC7620 Mini-sputter coater, a thin layer of quickly drying silver paste (silver in isobutyl ketone, TED PELLA, INC.) was painted onto both sides of each pellet generating the symmetrical cell Ag|Pellet|Ag. Using a Stanford Research RCL Bridge, AC electrical conductivity measurements for the pellets were made between the temperature of 298 and 338 K and at a frequency of 10 kHz (Model: SR-720). A Volta lab master radiometer (PGZ 301 model) and the Zsimpwin program were also utilized to evaluate the impedance inquiry for the pellets. An AC sine wave with amplitude of 10 mV and a frequency range of 100 kHz to 50 mHz were used to recognize impedance at ambient temperature. At room temperature, the constructed batteries were subjected to charge-discharge experiments using a battery tester (Bio-Logic MPG-205, France).

3. THE FINDINGS AND DISCUSSION

3.1. Structural Characteristics

3.1.1. Crystal structure

The XRD patterns of the LNMO, LNMO-Th, and LNMO-Th-PA specimens are presented in Fig. 1. The detected peaks are primarily correlated with the cubic spinel phase of LNMO with an Fd3m space group (JCPDS No. 89-0107) at 18.68°, 36.22°, 37.89°, 44.04°, 48.22°, 58.28°, 64.03°, and 67.87°. (111), (311), (222), (400), (331), (511), (440) and (531) are the matching crystal planes (hkl). A limited portion of Li$_x$Ni$_{1-x}$O$_2$, which vanished with Th-doping, was found in the LNMO sample at 2θ° equal to 36.8°, so it is possible to prevent the forming of these residues by doping with ions of transition metals [29]. Additionally, the lack of peaks (20 = 15.3, 39.7, 45.7, 57.5, and 65.68) supports the generated powders' disordered Fd3m structure [30]. Also supporting the dimensional support of the disordered spinel phase with Mn$^{4+}$ ions framework is the high-intensity ratio I(311)/I(400) of the samples in Table 1 [26, 31]. The electrochemical performance improved as the intensity ratio I(311)/I(400) was raised [25, 32]. Table 1 also includes a summary of additional crystallographic characteristics of the as-prepared materials, such as the lattice parameters (a) and cell volume (v). The lattice constants and cell volumes of the Th-doped LNMO are reported to be smaller than those of the pure LNMO, even though the ionic radius of Th$^{4+}$ (1.05 ) is greater than those of Mn$^{3+}$ (0.645A ) and Mn$^{4+}$ (0.53A ).
Table 1. Lattice characteristics and crystallite size of the specimens after calcination at 700° for three hours.

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>V(Å³)</th>
<th>I_{(311)}/I_{(400)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNMO</td>
<td>8.1734</td>
<td>546.01</td>
<td>0.89</td>
</tr>
<tr>
<td>LNMO-Th</td>
<td>8.1680</td>
<td>544.93</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Figure 1. XRD patterns of the (a) LNMO, (b) LNMO-Th, calcined at 750° for three hours and (c) LNMO-Th-PA after drying for 12 hours at 60 °C. “*” refers to the LixNi_{1-x}O_2 phase

3.1.2. FT-IR SPECTROSCOPY

The synthesized LNMO, LNMO-Th, and LNMO-Th-PA materials were each given an FTIR spectroscopic analysis to determine their characteristics. As seen in Fig. 2, the involvement of five distinct bands at around 620, 582, 554, 595, and 465 cm⁻¹ in the FT-IR spectra of both LNMO and LNMO-Th samples suggests the existence of a significant amount of cubic unstructured spinel phase with space group Fd-3m [34, 35]. Additionally, the extent of disordered in 16d octahedral sites increases since the intensity ratio between the peaks has increased at 620 cm⁻¹ and 582 cm⁻¹ (MnO and NiO band respectively) [20, 36]. As a result of quicker electrical conductivity, LNMO-Th samples
display a sizable amount of disordering with absolute Fd3m space group, indicating improved electrochemical behavior compared to pure LNMO spinel [25, 26]. Fig. 3 illustrates the LNMO-Th-PA composite's FTIR spectrum. The characteristic peaks arise at 1560 cm\(^{-1}\) for the quinoid ring's (C=C stretching mode), 1475 cm\(^{-1}\) for benzenoid rings' (C=C stretching mode), 1299 cm\(^{-1}\) and 1242 cm\(^{-1}\) for the C-N ring's stretching mode, and 1130 cm\(^{-1}\) for the N = quinoid ring's = N [37].

![Figure 2. FT-IR of the synthesized materials (LNMO and LNMO-Th) treated for 3 hours at 750 °C.](image)

![Figure 3. FT-IR of the synthesized nanopowders (LNMO, LNMO-Th and LNMO-Th-PA) calcined for 3 hours at 750 °C.](image)
3.2. Microstructural properties

TEM was used to describe the morphologies of the produced materials, as illustrated in Fig. 4. The granules of the LNMO and LNMO-Th samples indicate a semi-regular appearance with a variable range of particle sizes in Fig. 5a, b. However, Figure 5c shows that the LNMO-PANI nanocomposite has a reverse rough surface. Hence, this proves the addition of a uniform PANI layer on the surface of the LNMO-Th particles. The PANI layer has a thickness of about 4-6 nm and is very evenly distributed across the surface of the LNMO-Th particles, as seen in Fig. 5c. EDX pattern as shown in Fig. 5, confirms the makeup of each sample. Also, the samples' distribution of the elements (Ni, Th, Mn, N, C, and O) is uniform.

Figure 4. TEM image of (a) LNMO, (b) LNMO-Th, (c) LNMO-Th-PA and (d) thickness of polyaniline coating of LNMO-Th-PA composite.
3.3. XPS spectra

The XPS spectra in Fig. 6 are used to investigate the element valence changes in the LNMO and LNMO-Th materials. Mn 2p$_{3/2}$ XPS binding energies for Mn$^{3+}$ and Mn$^{4+}$ have been determined to be 641.9 and 643.2 eV, respectively [34, 35]. Compared to LNMO, the Mn 2p$_{3/2}$ XPS binding energy of LNMO-Th shows a positive shift in this research, emphasizing that the oxidation state of manganese (Mn) has increased and that Mn$^{3+}$ has decreased and oxidized to Mn$^{4+}$. The Ni 2p$_{3/2}$ XPS binding energies for Ni$^{2+}$ and Ni$^{3+}$, respectively, are 854.8 and 855.8 eV [33]. The binding energies (Ni 2p$_{3/2}$ XPS) of LNMO-Th negatively shifted. So, it can be believed that both Ni$^{2+}$ and Ni$^{3+}$ are viable in an octahedral environment [38]. The XPS spectra of Th 4f from LNMO-Th are shown in Fig. 6e.
According to the binding energies of Th 4f$_{5/2}$ and Th 4f$_{7/2}$, the two peaks at 346.7 eV and 338.2 eV, respectively, show that the Th has been integrated into the LiNi$_{0.5}$Mn$_{1.5}$O$_4$ lattice in LNMO-Th [39].

![Figure 6](image)

**Figure 6.** XPS spectra of the prepared materials (a, b) LNMO and (c, e) LNMO-Th, calcined at 750 for 3 hours.

### 3.4. Electronic conductivity of bulk materials

The EIS spectra (Nyquist and bode) for the symmetric Ag-electrodes and pellets sandwiched between them are shown in Fig. 7 and Fig. 8 in the range of frequencies from one mHz to one MHz at ambient temperature. According to the findings, each cell showed a normal one-semicircle shape, indicating that ionic conductivity was not a factor. For LNMO, LNMO-Th, and LNMO-Th-PA pellets, the levels of charge transfer resistance ($R_{ct}$) were 4.1, 3.5, and 2.7 kΩ, respectively. Such figures show
that the grains (bulk materials) rather than the borders are the source of the resistive action. The Arrhenius plot illustrating the relationship between AC conductivity (ln AC) and the reciprocal of absolute temperature (1000/T) at 10 kHz is shown in Fig. 9 [40, 41]. The trend line for the temperature range (30-65 °C) is straight, demonstrating that the AC conductivity matches the Arrhenius law above this level and is determined by (1):

$$\sigma_T = \sigma_0 \exp \left(-\frac{E_a}{k_B T}\right)$$

(1)

Where (E_a) stands for activation energy, (k_B) for the Boltzmann constant, and (\sigma_0) for a pre-exponential component. According to Table 2, the activation energies (E_a) of conduction for LNMO, LNMO-Th, and LNMO-Th-PA samples are respectively 0.21, 0.11, and 0.08 eV. As a result, the Th^{3+} doping lowers the activation energy of the LNMO material, improving its electronic conductivity. The temperature dependence of the dielectric constant (\varepsilon_r) and dielectric loss factor (tan \delta) at 10 kHz is shown in Figs. 10 and 11. The findings show that for the LNMO and LNMO-Th samples, the values of (\varepsilon_r) and (tan \delta) increased gradually, whereas they increased sharply for the LNMO-Th-PA sample above 50 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ln (\sigma_{AC})</th>
<th>tan (\delta)</th>
<th>(\varepsilon_r)</th>
<th>(R_{ct}), kΩ</th>
<th>E_a (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNMO</td>
<td>-5.7</td>
<td>2.16</td>
<td>134</td>
<td>4.1</td>
<td>0.21</td>
</tr>
<tr>
<td>LNMO-Th</td>
<td>-6.1</td>
<td>7.61</td>
<td>659</td>
<td>3.5</td>
<td>0.11</td>
</tr>
<tr>
<td>LNMO-Th-PA</td>
<td>-10.6</td>
<td>0.77</td>
<td>650</td>
<td>2.7</td>
<td>0.08</td>
</tr>
</tbody>
</table>

**Figure 7.** Nyquist plots of the prepared nanoparticles (LNMO, LNMO-Th, and LNMO-Th-PA) at ambient temperature, frequency range of 100 kHz to 50 MHz.
Figure 8. Bode plots of (LNMO, LNMO-Th, and LNMO-Th-PA) at ambient temperature.

Figure 9. Arrhenius plot of (ln $\sigma_{AC}$) versus $[(1000/T) \text{ K}^{-1}]$ of the prepared nanoparticles (LNMO, LNMO-Th, and LNMO-Th-PA) at 10 kHz for the pellets.
Figure 10. The temperature dependence of the dielectric loss factor (tan δ) of the prepared nanoparticles (LNMO, LNMO-Th, and LNMO-Th-PA).

Figure 11. A Plot of the temperature dependence of the dielectric constant (εr) at 10 kHz.

3.5. Charge/discharge performance

The examined nanoparticles (LNMO, LNMO-Th, and LNMO-Th-PA) underwent a charge/discharge process at voltages between 3.0 and 5.2 V. The outcome showed that LNMO has an initial discharge capacity of around 110mAh/g (Fig. 12). Adding Th particles improves the
electrochemical performance of the LNMO-Th, where the discharge capacity was increased to about 127 mAh/g. Also, the introduced polyaniline particles (LNMO-Th-PA) composite's creation increased the first discharge capacity to 148 mAh/g [42]. Table 3 listed the initial discharge capacity recorded for different polyaniline composites as cathode materials in many previous studies in the literature.

![Figure 12](image.png)

**Figure 12.** Comparison of charge/discharge performance of the prepared nanoparticles.

**Table 3.** The initial discharge capacity for different polyaniline composites in the literature.

<table>
<thead>
<tr>
<th>Reference</th>
<th>The initial discharge capacity (mAhg⁻¹)</th>
<th>Reference</th>
<th>The initial discharge capacity (mAhg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td>148</td>
<td>[47]</td>
<td>125.3</td>
</tr>
<tr>
<td>[43]</td>
<td>160</td>
<td>[48]</td>
<td>183.4</td>
</tr>
<tr>
<td>[44]</td>
<td>142.4</td>
<td>[49]</td>
<td>294</td>
</tr>
<tr>
<td>[45]</td>
<td>100</td>
<td>[50]</td>
<td>144</td>
</tr>
<tr>
<td>[46]</td>
<td>121</td>
<td>[51]</td>
<td>115</td>
</tr>
</tbody>
</table>

4. CONCLUSION

LiNi₀.₅Mn₁.₅O₄ (LNMO), LiNi₀.₄₅Th₀.₀₅Mn₁.₅O₄ (LNMO-Th) and LiNi₀.₄₅Th₀.₀₅Mn₁.₅O₄/Polyaniline composite (LNMO-Th-PA) was prepared. The lattice constants and cell volumes of the Th-doped LNMO are reported to be smaller than those of the pure LNMO. The optical properties show that all samples have low band gap values. Thus, the synthesized materials are semiconductor material and they can be used in photoelectric devices. The electrochemical
performance of LNMO-Th is much better than the un-doped sample LNMO and LNMO-Th-PA samples.

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References


